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(33)

EP 1 254 930 A2

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:  
06.11.2002 Bulletin 2002/45

(51) Int Cl.7: C09C 3/10, C09C 1/56.

(21) Application number: 02009674.9

(22) Date of filing: 29.04.2002

(84) Designated Contracting States:  
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU  
MC NL PT SE TR  
Designated Extension States:  
AL LT LV MK RO SI

- Yano, Tetsuya  
Tokyo (JP)
- Kozaki, Shinya  
Tokyo (JP)
- Hanma, Tsutomu  
Tokyo (JP)

(30) Priority: 27.04.2001 JP 2001131824  
10.07.2001 JP 2001210060

(71) Applicant: CANON KABUSHIKI KAISHA  
Ohta-ku, Tokyo (JP)

(74) Representative: Weser, Wolfgang, Dr. Dipl.-Phys.  
Weser & Kollegen,  
Patentanwälte,  
Radeckestrasse 43  
81245 München (DE)

(72) Inventors:  
• Nomoto, Tsuyoshi  
Tokyo (JP)

(54) Particles for electrophoresis, a production method thereof and a display using the particles

(57) Electrophoretic particles for electrophoretic display having excellent dispersibility and dispersion stability with time for insulating media, and being protected against coagulation, settling and the like, a process for production of the electrophoretic particles having high versatility for pigments to be used in response to a

full-color display, and an electrophoretic display device using the electrophoretic particles that has an excellent memory property and is highly reliable are provided. The electrophoretic particles are formed using as at least a part of structure a pigment with at least a part of the surface covered with polyhydroxyneanoate.

FIG. 1A

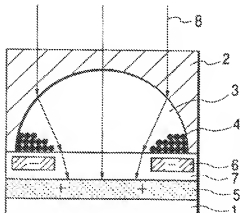
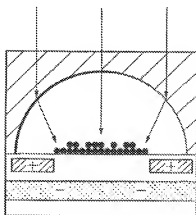
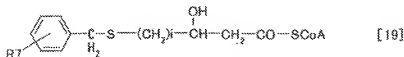


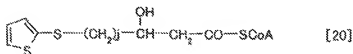
FIG. 1B



$-\text{CH}(\text{CH}_3)_2$  and  $-\text{C}(\text{CH}_3)_3$  corresponding to R6 in the monomer unit expressed by the above described Formula [8] wherein R' represents any of a hydrogen atom (H), Na, K,  $-\text{CH}_3$  and  $-\text{C}_2\text{H}_5$ , and R'' represents any of  $-\text{OH}$ ,  $-\text{ONa}$ ,  $-\text{OK}$ , a halogen atom,  $-\text{OCH}_3$  and  $-\text{OC}_2\text{H}_5$ .)



(wherein  $-\text{SCoA}$  represents a coenzyme A bound to alkanolic acid, j represents an integer number of 1 to 7 corresponding to i in the monomer unit expressed by the above described Formula [9], and R7 represents any one selected from the group consisting of a hydrogen atom (H), halogen atom,  $-\text{CN}$ ,  $-\text{NO}_2$ ,  $-\text{COOR}'$  and  $-\text{SO}_2\text{R}'$  corresponding to R7 in the monomer unit expressed by the above described Formula [9] wherein R' represents any of a hydrogen atom (H), Na, K,  $-\text{CH}_3$  and  $-\text{C}_2\text{H}_5$ , and R'' represents any of  $-\text{OH}$ ,  $-\text{ONa}$ ,  $-\text{OK}$ , a halogen atom,  $-\text{OCH}_3$  and  $-\text{OC}_2\text{H}_5$ .)



(wherein  $-\text{SCoA}$  represents a coenzyme A bound to alkanolic acid, and j represents an integer number of 1 to 9 corresponding to j in the monomer unit expressed by the above described Formula [10].)

[0027] Furthermore, specific examples of the above described halogen atom may include fluorine, chlorine and bromine. In addition, the above described chromophoric group is not particularly limited as long as its 3-hydroxyacyl CoA body can be subjected to catalytic action of the PHA synthesizing enzyme, but it is more desirable that a methylene chain having 1 to 5 carbon atoms exists between the carboxyl group with CoA bound thereto and the chromophoric group in the 3-hydroxyacyl CoA molecule if considering steric hindrance that may occur during synthesis of a polymer. In addition, if the optical absorption wavelength of the chromophoric group is in the visible range, a colored micro-encapsulated pigment can be obtained even if an extender pigment is used. Examples of such chromophoric groups may include nitroso, nitro, azo, diarymethane, triarylmethane, xanthene, acridine, quinoline, methine, thiazole, indamine, indophenol, lactone, aminoketone, hydroxyketone, stilbene, azine, oxazine, thiazine, anthraquinone, phthalocyanine and indigoid.

[0028] For PHA to be used in the present invention, random copolymers and block copolymers each including the above described plurality of monomer units can also be used, thus making it possible to control properties of PHA and provide a plurality of functions using the properties of respective monomer units and contained functional groups, to realize new functions using interaction between functional groups, and so on. In addition, it is also possible to synthesize a block copolymer of any order and composition on the surface of the pigment by selecting as appropriate the amount and order in which 3-hydroxyacyl CoA as a substrate is added. In addition, as required, chemical modification and the like may also be made after or during synthesis of PHA.

[0029] It is also possible to change the composition of the monomer unit of PHA in the direction extending from the inside of the pigment to the outside thereof by changing with time the composition such as type and concentration of 3-hydroxyacyl CoA as a substrate, for example. Thereby, for example, if it is necessary to form a cover structure with PHA having a low affinity for the pigment, the substrate is first covered with PHA having a high affinity for the substrate, and the composition of the monomer unit of PHA having a high affinity for the pigment is changed to the composition of the monomer unit of desired PHA in the direction extending from the inside toward the outside, or in the vertical direction to form, for example, a multi-layer structure or gradient structure, thereby making it possible to form a PHA cover with its bonding to the pigment enhanced.

[0030] In addition, by introducing a graft chain in PHA on the surface of the micro-encapsulated pigment, a micro-encapsulated pigment having properties derived from the graft chain can be obtained. In addition, by having PHA on the surface of the pigment crosslinked, a micro-encapsulated pigment having excellent mechanical strength can be obtained.

[0031] Furthermore, PHA synthesized by a PHA synthesizing enzyme, which is used in the structure of the present invention, is generally an isotactic polymer constituted only by a R-configuration.

[0032] 3-hydroxyacyl CoA as a synthesis substrate for PHA can be synthesized for use by a method appropriately selected from an in vitro synthesis method using enzymes, an in vivo synthesis method using organisms such as

8.0) in the concentration of 10 mg/ml, and Reagent 4: 5,5'-dithiobis-(2-nitrobenzoic acid) is dissolved in a 0.1 M Tris hydrochloric buffer (pH 8.0) in the concentration of 2.0 mM. First reaction (PHA synthesizing reaction): 100  $\mu$ l of Reagent 1 is added in 100  $\mu$ l of sample (enzyme) solution and mixed together, and is pre-incubated at 30°C for 5 minutes. 100  $\mu$ l of Reagent 2 is added thereto and mixed together, and is incubated at 30°C for 1 to 30 minutes, followed by adding thereto Reagent 3 to stop the reaction. Second reaction (reaction of coloring free CoA): the first reaction solution of which reaction has been stopped is subjected to centrifugation (15,000  $\times$  g, 10 minutes), and 500  $\mu$ l of Reagent 4 is added in 500  $\mu$ l of supernatant liquid of this solution, and is incubated at 30°C for 15 minutes, followed by measuring an absorbance at 412 nm. Calculation of enzyme activity: the amount of enzyme for releasing 1  $\mu$ mol of CoA per minute is defined as one unit (U).

<Process for producing electrophoretic particles>

[0048] One example of process for production of electrophoretic particles containing micro-encapsulated pigments of the present invention may be a process comprising at least steps of (1) dispersing pigments on an aqueous medium, (2) fixing a PHA synthesizing enzyme to the dispersed pigment, (3) adding 3-hydroxyacyl CoA as a substrate, (4) carrying out a PHA synthesizing reaction and (5) collecting micro-encapsulated pigment particles covered with PHA as electrophoretic particles, and processing the same as an electrophoretic particle dispersion system for use in an electrophoretic display device.

[0049] The step of dispersing the pigment on the aqueous medium is conducted by adding one or more selected pigments in the aqueous medium, and carrying out dispersion processing, followed by classifying the pigment in a desired range of particle size if necessary.

[0050] The pigment for use in the present invention may be an organic or inorganic pigment, but is preferably excellent in heat resistance and light resistance. Examples of organic pigments may include azo-based, phthalocyanine-based, benzimidazolone-based, quinacridone-based, isoidolone-based, pyrazolone-based, dibromanthrone-based, indanthrone-based, anthrapyrimidine-based, flavanthrone-based, perylene-based, perynone-based, quinophthalone-based, phthalone-based, thionindigo-based, indigo-based, diazine-based, anthraquinone-based, xanthene-based, methine-based and azomethine-based pigments, and condensation polycyclic pigments including other metal complex pigments. Examples of inorganic pigments may include Miron blue, iron oxide, cobalt purple, manganese purple, ultramarine blue, Prussian blue, cobalt blue, cellularine blue, pyridine, emerald green, cobalt green and red iron oxide, and one or two types thereof are appropriately selected and used. The above pigments may be used after being subjected to a various kinds of well known surface treatments. Examples of surface treatments include surfactant treatment, coupling treatment and pigment derivative treatment.

[0051] Dispersion processing may be carried out using a homo mixer, a horizontal mini mill, a ball mill, a roll mill, a sand grinder, a milling machine, a supersonic operation or the like. In addition, the dispersion may be carried out by a method in which mixtures are passed through a large number of nozzles under a hydraulic pressure of at least 1000 psi (about 70.3 kg/cm<sup>2</sup>) in a liquid jet interaction chamber.

[0052] It is desirable that the pigment is dispersed in a single dispersion state in the range of from 0.05  $\mu$ m to 4.5  $\mu$ m for the particle size of the dispersed pigment. If the particle size of the dispersed pigment is not fallen in a desired range, classification by filtration and sedimentation processes can be carried out to make an adjustment.

[0053] The particle size of the dispersed pigment can be measured by known methods such as an absorbance method, a static light-scattering method, a dynamic light-scattering method and a centrifugal sedimentation method, and for example, an apparatus for measuring particle sizes such as Coulter counter multi-sizer may be used.

[0054] The composition of the aqueous medium for synthesis of PHA in this step may be any composition that allows the pigment to be dispersed in a desired state, and does not interfere the subsequent steps of fixing the enzyme to the pigment and carrying out the PHA synthesizing reaction, but the composition may be adjusted into a composition allowing the activity of the PHA synthesizing enzyme to be exerted in order to simplify the subsequent steps. As the composition allowing the activity of the PHA enzyme to be exerted, for example, a buffer may be used. For the buffer, general buffers for use in biochemical reactions, for example, acetate buffers, phosphate buffers, potassium phosphate buffers, 3-(N-morpholino) propane sulfonate (MOPS) buffers, N-tris (hydroxymethyl) methyl-3-aminopropane sulfonate (TAPS) buffers, trischloride buffers, glycine buffers, and 2-(cyclohexylamino) ethanesulfonate (CHES) buffers are suitably used. The concentration of the buffer allowing the activity of the PHA synthesizing enzyme to be exerted may be a general concentration, namely in the range of from 5 mM to 1.0 M, but is preferably in the range of from 10 to 200 mM. Also, an adjustment is made so that pH is in the range of from 5.5 to 9.5, preferably from 7.0 to 8.5, but the possibility is not excluded that a pH condition is set in a range other than the above described range depending on the most suitable pH and pH stability of a PHA synthesizing enzyme to be used.

[0055] In addition, for maintaining a pigment dispersion condition in the aqueous medium, a suitable surfactant may be added as long as the surfactant has a type and concentration not interfering the subsequent steps, and has a type and concentration not interfering the purpose of the colored composition of the present invention. Examples of the

omer unit of PHA covering the pigment in this direction extending from the inside toward the outside of the pigment. d (11)  
 [0074] The form of this pigment with the monomer unit composition changed may be, for example, a form in which d (12)  
 the change of the composition of the PHA cover is continuous, and the pigment is covered with one layer of PHA having a gradient of composition formed in this direction extending from the inside toward the outside. The production method may be, for example, a method in which 3-hydroxyacyl CoA of different composition is added in the reaction solution while synthesizing PHA.

[0075] In addition, as another form, there may be a form in which the composition of the PHA cover is changed by stages, and PHA of different compositions covers the pigment in multiple layers. The production method for this form may be a method in which PHA is synthesized with a certain composition of 3-hydroxyacyl CoA, followed by coating the pigment under preparation from the reaction solution on a temporary basis using centrifugation or the like, and adding thereto a reaction solution of 3-hydroxyacyl CoA of different composition again, and so on.

[0076] The step of carrying out a PHA synthesis reaction is carried out by preparing the composition of reaction solution so that a composition allowing activity of the PHA synthesizing enzyme to be exerted can be obtained if the composition of reaction solution has not been prepared till the previous step, and adjusting the reaction temperature and reaction time, in order that a micro-capsulated pigment having a desired shape can be obtained by PHA to be synthesized.

[0077] The concentration of the buffer for the reaction solution allowing the activity of the PHA synthesizing enzyme to be exerted may be a general concentration, namely a concentration in the range of from 5 mM to 1.0 M, but is desirably a concentration in the range of from 10 to 200 mM. For pH, an adjustment is made so that the pH is in the range of from 5.5 to 9.0, preferably from 7.0 to 8.5, but the possibility is not excluded that a pH condition is set in a range other than the above described range depending on the most suitable pH and pH stability of a PHA synthesizing enzyme to be used.

[0078] The reaction temperature is set as appropriate depending on the property of the PHA synthesizing enzyme to be used, but may be set normally at 4 to 50 °C, preferably at 20 to 40 °C. However, the possibility is not excluded that a temperature condition is set in a range other than the above described range depending on the most suitable temperature and heat resistance of a PHA synthesizing enzyme to be used.

[0079] The reaction time is appropriately selected and set within the range of normally from 1 minute to 24 hours, preferably from 30 minutes to 3 hours depending on stability, etc., of the PHA synthesizing enzyme to be used.

[0080] The micro-capsulated pigment is obtained by this step, but the structure of monomer units of PHA constituting the microcapsule can be determined by extracting PHA from the micro-capsulated pigment with chloroform, and thereafter carrying out composition analysis by gas chromatography or the like, or using a time-of-flight secondary ion mass spectrometer (TOF-SIMS) and an ion sputtering technique.

[0081] The molecular weight of PHA is not particularly limited, but the number-average molecular weight is desirably in the range of from 1,000 to 10,000,000, more preferably from 3,000 to 1,000,000 for maintaining strength of the micro-capsulated pigment, and providing a stable amount of charge. The molecular weight of PHA may be measured by GPC (gel permeation chromatography) after PHA is extracted from the micro-capsulated pigment with chloroform.

[0082] Also, in the method of producing the micro-capsulated pigment according to the present invention, density of the pigment in the microcapsule can be increased because the pigment can be directly covered with PHA. On the other hand, however, it is required that the amount of PHA covering the pigment should be increased to enhance dispersibility and mechanical strength of the micro-capsulated pigment, and consequently, the amount of PHA covering the pigment is, for example, in the range of from 1 to 30% by mass, preferably from 1 to 20% by mass, more preferably 1 to 15% by mass of the weight of the pigment.

[0083] The particle size of the micro-capsulated pigment obtained by the above step is 50 µm or smaller, preferably 10 µm or smaller, more preferably 0.01 to 10 µm. The particle size of the micro-capsulated pigment can be measured by known methods such as an absorbance method, a static light scattering method, a dynamic light scattering method and a centrifugal sedimentation method, and for example, an apparatus for measuring particle sizes such as a Coulter counter multi-sizer may be used.

[0084] In addition, the micro-capsulated pigment obtained by this step may be subjected to various kinds of secondary treatments and processing such as chemical modification before being used.

[0085] For example, a micro-capsulated pigment having further useful functions and properties can be obtained by subjecting PHA on the surface of the pigment to chemical modification. For example, a graft chain is introduced, whereby a micro-capsulated pigment having various kinds of properties derived from the graft chain can be obtained. If polyisoxane as described later is introduced as a graft chain, for example, a micro-capsulated pigment having improved mechanical strength, dispersibility, weather resistance, water repellency (resistance), heat resistance and the like can be obtained, and storage stability and weather resistance of electrophoretic particles using the pigment can be improved. In addition, if the micro-capsulated pigment is used in an electrophoretic display device with dyes contained in an insulating medium, it can be expected that contamination of electrophoretic particles with dyes is curbed. In addition, by having PHA on the surface of the pigment crosslinked, mechanical strength, chemical resistance, heat

<223> Description of Artificial Sequence:Primer for PCR  
multiplication

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39

<210> 14

<211> 30

<212> DNA

<213> Artificial Sequence

<220>

<223> Description of Artificial Sequence:Primer for PCR  
multiplication

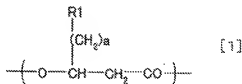
<400> 14

cgatctcag gagcagcgc acgtaagtc

39

# Claims

1. An electrophoretic particle comprising a pigment at least a part of the surface of which pigment is covered with polyhydroxyalkanoate
2. The electrophoretic particle according to claim 1, wherein said polyhydroxyalkanoate is comprised of at least one selected from the group consisting of monomer units expressed by formulas [1] to [10].



(wherein symbol "a" represents an integer, and the combination of R1 and "a" is selected from the group consisting of a combination of a hydrogen atom and any one integer selected from the group consisting of 5 to 10;

a combination of a halogen atom and any one integer selected from the group consisting of 1 to 10;

a combination of a chromophoric group and any one integer selected from the group consisting of 1 to 10;

a combination of a carboxyl group or a salt thereof and any one integer selected from the group consisting of 1 to 10; and

a combination of

